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AMORPHOUS MAGNETIC INSULATORS FOR MICROWAVE DEVICE APPLICATIONS

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SUMMARY

Results of our studies on thin films of amorphous magnetic oxides are summarized in this report. The main emphasis of the program was on the preparation and magnetic characterization of amorphous $BiFeO_3$ films substituted with nonmagnetic perovskites, zinc ferrite, copper ferrite and calcium ferrite. Magnetization and ferromagnetic resonance techniques were used to study the magnetic structure in as-sputtered films, the onset of a magnetically ordered state in annealed samples, and the effects of crystallization on magnetic parameters. The main accomplishments of our efforts are: (i) amorphous insulators with the highest saturation magnetization ever achieved were synthesized, (ii) anisotropic amorphous magnets were realized in perovskite-spinel systems and (iii) the nature and composition of magnetically ordered clusters that give rise to a spontaneous magnetic moment were identified in some compounds.

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I. INTRODUCTION:

A two-year research program on magnetic ordering in amorphous oxides, funded by the Office of Naval Research, was initiated in January 1990. The basic objectives of the program were to prepare noncrystalline materials by rf sputtering techniques and to characterize the thin films by static and dynamic magnetic measurements. The research was aimed at achieving a high saturation magnetization and low high frequency losses in such a new class of materials for possible use in high frequency devices. Our efforts have resulted in amorphous oxides with the highest magnetization ever reported for such materials and the first observation of a large uniaxial or planar anisotropy in some compounds.

The crystalline $BiFeO_3$ is an antiferromagnet at room temperature. The sample shows a ferrimagnetic character in the amorphous state when substituted with magnetic or nonmagnetic compounds. The films were prepared by rf sputtering. Techniques including x-ray diffraction, scanning electron microscopy, and energy dispersive x-ray spectroscopy for structural characterization and static magnetization and ferromagnetic resonance for magnetic characterization were used. Further details on the results of these measurements are provided in Section II. Section III lists all publications on the grant. Section IV lists personnel supported.

II. RESULTS:

Amorphous oxides mainly containing $BiFeO_3$ and a magnetic or nonmagnetic substitution were examined. A ferrimagnetic character was observed in as-deposited or annealed films of (i) $BiFeO_3$-ABO_3, (ii) $BiFeO_3$-$ZnFe_2O_4$, (iii) $BiFeO_3$-$CuFe_2O_4$, (iv) $BiFeO_3$ - $CaFe_2O_4$, and (v) $CuFe_2O_4$. Important magnetic parameters for the films are listed in Table II-1. Details on sample preparations and structural and magnetic characterization are provided in the subsequent subsections.

Table II-1: Room temperature values of the saturation induction $4\pi M$, the uniaxial or planar anisotropy field H_u, and the ferromagnetic resonance line-width ΔH, and the curie temperature T_c for either as-deposited or annealed amorphous oxides prepared by rf sputtering techniques.

system	$4\pi M$ (G)	H_u (Oe)	ΔH (Oe)	T_c (°C)
(1-x) $BiFeO_3$ - x ABO_3				
AB = BaTi	200 - 1600	–	--	380 - 440
PbTi	100 - 450	–	--	360 - 450
PbZr	400 - 3800	–	--	440 - 490
(1-2x) $BiFeO_3$ - x $ZnFe_2O_4$	500 - 1900	400	200 - 300	330
(1-2x) $BiFeO_3$ - x $CuFe_2O_4$	150 - 3000	40 - 2700	500 - 1100	480 - 500
(1-2x) $BiFeO_3$ - x $CaFe_2O_4$	350 - 1000	200 - 300	170 - 300	300 - 400
$CuFe_2O_4$	750	500	600	450

II-A: SAMPLE PREPARATION:

A single target rf sputtering system with a Kurt Lesker Tours 2C magnetron gun was used for preparations of thin amorphous films of substituted $BiFeO_3$ compounds. A 2 inch dia. polycrystalline sintered target prepared by standard ceramic techniques was mounted in the magnetron gun. The system was evacuated to a base pressure of 10^{-5} Torr. The sputtering was carried out in pure argon, pure oxygen, or 50% oxygen and 50% argon atmospheres at a pressure of 1 mTorr or 25-40 mTorr and an rf power of 150W at 13.6 MHz. Films were deposited on Corning 7059 glass and silicon substrates mounted on a rotating unheated platform placed below the target. Samples with thickness on the order of 1 μm were obtained for a sputtering time of 90-120 min.

Structural characterization on the films were carried out at Energy Conversion Devices, Inc., Troy, Michigan. Film thickness measurements were performed with a stylus profilometer. Investigations on the structure and chemical composition were done with x-ray diffractometry and energy dispersive x-ray spectrometry, respectively. The deposition rate was found to be dependent on the sputtering atmosphere, pressure, and target composition. A relatively thick oxygen deficient film was obtained in Ar-atmospheres. The sputtering rate decreased when the pressure was increased. The film composition deviated by a maximum of ±10% in Fe and Bi contents and by ±20% in AB, Zn, or Cu content. In the discussion to follow, we use the target composition for convenience. The as-deposited films were found to be amorphous from x-ray diffraction studies.

Facilities used for magnetic characterization of amorphous samples include a Faraday balance, vibrating sample magnetometer, ac susceptometer, and ferromagnetic resonance spectrometers operating at 9 GHz. High-field magnetization studies on representative samples were done with a 5 Tesla SQUID magnetometer available at West Virginia University. The anisotropy fields were estimated from data on static magnetization and FMR parameters.

II.B. $BiFeO_3$ - ABO_3 COMPOUNDS:

Our studies show a ferrimagnetic character in the amorphous (a-) system (1-x) $BiFeO_3$ - x ABO_3 for x = 0.1 - 0.9. Here, ABO_3 is a ferro-/antiferroelectric perovskite such as $BaTiO_3$, $PbTiO_3$, and $PbZrO_3$. Measurements were done on 1 μm thick films sputtered in 50% oxygen + 50% argon atmospheres. The important magnetic parameters are listed in Table II-1. Results of our investigation are summarized below.

(i) As-deposited films are paramagnets at room temperature for all x-values. The films develop a ferrimagnetic moment when annealed at temperatures T_a = 100-750°C. Data on the magnetization M versus T_a for samples substituted with

ABO_3 are shown in Fig.II-1. For $T_a < 500°C$, M does not show any dependence on T_a. With further increase in T_a, M begins to increase and shows a maximum at 650 - 725°C, depending on the x-value. For higher T_a-values, M decreases.

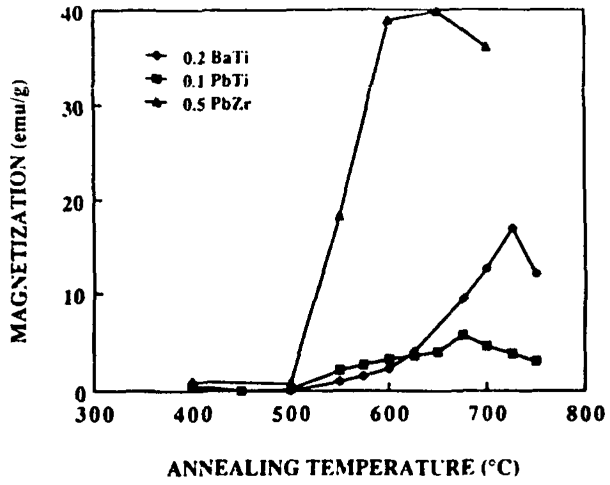

Fig.II-1: Room temperature magnetization measured at 6 kOe versus annealing temperature T_a data for films of $BiFeO_3$ substituted with 0.2 $BaTiO_3$, 0.1 $PbTiO_3$, and 0.5 $PbZrO_3$. The samples were annealed in air at T_a for 60 minutes.

(ii) The highest magnetization of 40 emu/g, corresponding to a saturation induction <u>$4\pi M$ of 3.8 kG</u> was achieved for the film containing 0.5 $PbZrO_3$. The $4\pi M$-values are comparable to that for spinel and hexagonal ferrites and are larger than for yttrium- and rare-earth iron garnets.

(iv) The effects of high temperature annealing on the crystal structure of the films were studied through x-ray diffraction measurements. Results of such studies on a representative sample, the film with 0.5 $PbZrO_3$, are shown in Fig.II-2. The figure shows the x-ray diffraction pattern for the as-deposited sample and for films annealed at 650°C and at 700°C. It is obvious from Fig.II-2 that the film retains the x-ray amorphous structure up to the annealing temperature at which M is a maximum. For higher T_a-values, one observes evidence for crystallization which accompanies the decrease in M. Several phases including $BiFeO_3$ and Fe_2O_3 were present in crystallized samples. The crystallization temperature for the films is larger than the Curie temperature listed in Table II-1.

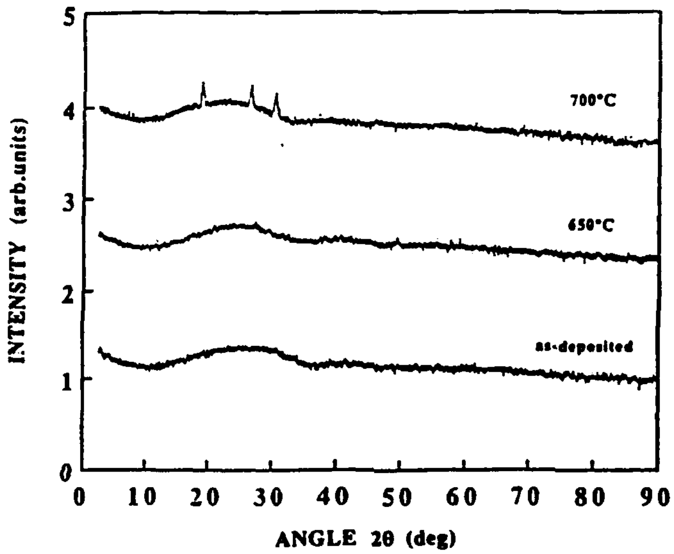

Fig.II-2: x-ray diffraction data for as-deposited and annealed samples of 0.5 $BiFeO_3$ - 0.5 $PbZrO_3$.

"Magnetic properties of amorphous BiFeO3 - PbZrO3 sputtered films," B. Uma Maheshwar Rao, G. Srinivasan, V. Suresh Babu, and M. S. Seehra, J. Appl. Phys. 69, 5463 (1991).
"Effects of high temperature annealing on amorphous BiFeO3 with nonmagnetic substitutions," B. Uma Maheshwar Rao and G. Srinivasan, Appl. Phys. Lett. 59, 372 (1991).

II-C: BiFeO3 - ZnFe2O4 COMPOUNDS:

Studies on rf sputtered amorphous compounds (1-2x) $BiFeO_3$ - x $ZnFe_2O_4$ for x = 0 to 0.5 led to the first observation of a ferrimagnetic behavior with an uniaxial anisotropy in the compound. The as-deposited amorphous films were paramagnets for all x-values. The samples developed a ferrimagnetic moment and an uniaxial anisotropy on annealing in air at high temperatures. The range of magnetization for this compound is listed in Table II-1. A maximum 4πM of 1900 G at room temperature was obtained for the sample with x = 0.3.

Hysteresis loop measurements showed a soft-magnetic character for the films. Figure II-3 shows such data at room temperature for H parallel and perpendicular to the plane of a film with x = 0.125 and annealed at 500°C. The coercive force varies from 90 Oe for H parallel to the film plane to 180 Oe for the perpendicular orientation. The linear increase in M for H above 1 kOe may be attributed to *coexisting paramagnetic clusters in the sample.*

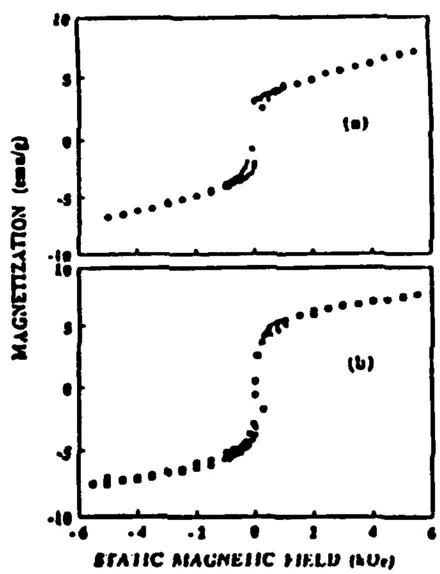

Fig.II-3: Data on the static field H dependence of room temperature magnetization for a sample of 0.75 $BiFeO_3$ - 0.125 $ZnFe_2O_4$ annealed at 500°C for H (a) parallel and (b) perpendicular to the film plane.

Figure II-4 shows the temperature dependence of 4πM for a series of samples annealed at 650-700°C. Since the amount of Fe in the samples is independent of x, it is clear form the data that the magnetization depends sensitively on the amount of nonmagnetic Zn in the sample. The measured T_C is about 600±10 K and is lower than the crystallization temperature. The absence of any systematic variation in T_c with x indicates that high temperature annealing results essentially in the formation of a specific type of magnetically ordered clusters in all Zn substituted samples.

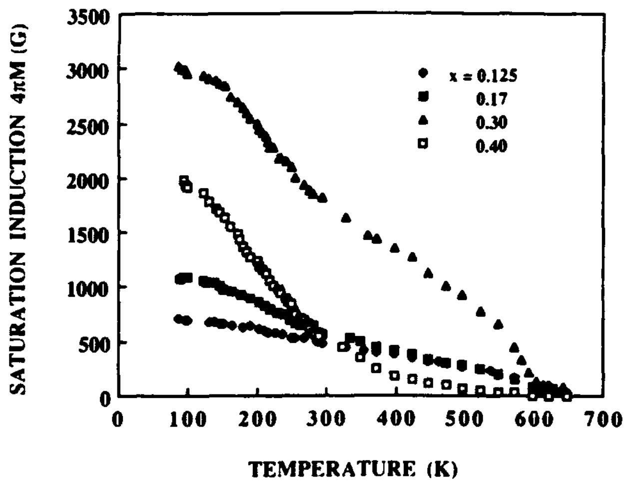

Fig.II-4: Saturation induction versus temperature data for samples of (1-2x) $BiFeO_3$ - x $ZnFe_2O_4$ annealed at 650-700°C.

One can obtain some information on the nature of clusters in the films from the data in Fig.II-4. The expected magnetic moment n per formula unit in a- (1-2x) $BiFeO_3$ - x $ZnFe_2O_4$ for a parallel alignment of Fe^{3+} ions is 5 μ_B at 0K, independent of the x-values, and is a factor of 5-10 larger than the moment at low temperatures in Fig.II-4. Therefore, the relatively small magnetization can be attributed to clusters consisting of ferrimagnetically coupled iron ions. The fact that the Curie temperature is independent of x indicates that the dominant superexchange interactions between magnetic ions within clusters are not significantly altered by the amount of Zn.

The presence of an uniaxial anisotropy field in the amorphous samples was clearly evident from ferromagnetic resonance studies. The measurements were performed at 9.2 GHz for applied static fields parallel and perpendicular to the sample plane. Data on the resonance fields for these two configurations were used to estimate the effective saturation induction $4\pi M_{eff} = 4\pi M - H_u$, where H_u is the uniaxial anisotropy field. One can then determine H_u-values from FMR data on $4\pi M_{eff}$ and static magnetization results on $4\pi M$. Results of such studies for a representative sample are shown in Fig.II-5.

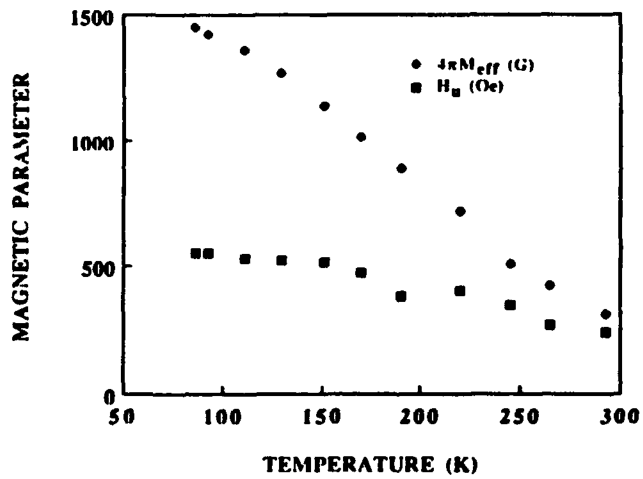

Fig.II-5: Variation of the effective magnetization $4\pi M_{eff}$ with temperature obtained from ferromagnetic resonance measurements at 9.2 GHz on an annealed sample of 0.2 $BiFeO_3$ - 0.4 $ZnFe_2O_4$. The perpendicular anisotropy field H_u was determined from $4\pi M_{eff}$-values and data on $4\pi M$ in Fig.II-4.

"Magnetic ordering in amorphous films of $BiFeO_3$ - $ZnFe_2O_4$," B. Uma Maheshwar Rao and G. Srinivasan, Phys. Rev. B 44, 395 (1991).

"Effects of sputtering atmospheres on magnetic properties of amorphous films of $BiFeO_3$ - $ZnFe_2O_4$," B. Uma Maheshwar Rao and G. Srinivasan, in press, Journal of Magnetism and Magnetic Materials.

II-D: $BiFeO_3$ - $CuFe_2O_4$ COMPOUNDS

A ferrimagnetic behavior characterized by an uniaxial anisotropy was observed through static and high frequency measurements in rf sputtered films of (1-2x) $BiFeO_3$ - x $CuFe_2O_4$ for x = 0 - 0.5. The most important results of our studies are as follows:

(i) the as-sputtered film with x = 0.5, pure copper ferrite, show a ferrimagnetic character with an in-plane anisotropy field at room temperature.

(ii) Unannealed samples with x = 0.1 - 0.4 are paramagnetic and annealed samples are ferrimagnetic with an uniaxial anisotropy. A maximum in the magnetization occurs for T_a = 500-600°C. Phases such as CuO and $Bi_2Fe_4O_9$ are formed when the samples are crystallized and the crystallization temperature is higher than the T_c-value of 480-500°C.

(iii) The largest $4\pi M$- value of 3 kG at room temperature is observed for the sample with x = 0.4. A soft-magnetic nature with a coercive force less than 10 Oe is evident from hysteresis loop studies.

(iv) The uniaxial anisotropy field increases with x, from 40 Oe for x = 0.1 to 2.7 kOe for x = 0.4 at room temperature.

(v) A positive identification of the nature and composition of magnetically ordered clusters in annealed samples was possible from the data on the Curie temperature, low temperature magnetization, and g-value. The T_c-value of 480-500°C, the magnetization of 1.1-1.3 μ_B per copper ion, and the g-value of 2.1-2.3 are in excellent agreement with the values expected for copper ferrite. Thus the amorphous clusters have a composition and spin structure similar to $CuFe_2O_4$.

"Static and high frequency magnetic properties of amorphous $BiFeO_3$ - $CuFe_2O_4$ compounds," B. Uma Maheshwar Rao and G. Srinivasan, J. Appl. Phys. 70, 6317 (1991).

"Magnetization and ferromagnetic resonance studies on rf sputtered amorphous $BiFeO_3$ - $CuFe_2O_4$ compounds," B. Uma Maheshwar Rao and G. Srinivasan, in press, Journal of Magnetism and Magnetic Materials.

II-E: $BiFeO_3$ - $CaFe_2O_4$ COMPOUNDS:

Magnetic properties of amorphous compounds with the composition $(Bi_2O_3)_{0.5-x}\,(Fe_2O_3)_{0.5}\,(CaO)_x$ were studied for samples with x = 0 - 0.5. As-sputtered samples were x-ray amorphous and paramagnetic at room temperature. When annealed in air at temperatures T_a, films *with* Ca show evidence for the onset of a long range order. The room temperature saturation induction $4\pi M$ and the Curie temperature for the samples were in the range 350 - 1000 G and 600 - 750 K, respectively, depending on the x-value.

Ferromagnetic resonance studies were performed at x-band frequencies to determine the the anisotropy filed, line-width and the gyromagnetic ratio. The amorphous films with x = 0.1 - 0.4 show a uniaxial anisotropy perpendicular to the film plane. However, one observes a planar anisotropy character in the film with x = 0.5. The smallest line-width FMR in amorphous compounds, about 170 Oe at room temperature, was observed for x = 0.4 samples.

"Magnetic properties of amorphous films of Bi_2O_3-Fe_2O_3-CaO," B. Uma Maheshwar Rao and G. Srinivasan, paper to be presented at INTERMAG'92. The manuscript if accepted will be published in IEEE Trans. Magn. 1992.

II-F: COPPER FERRITE:

We observed a long range magnetic order with planar anisotropy in *as-deposited* films of amorphous copper ferrite prepared by rf sputtering techniques. Data on the temperature dependence of the saturation magnetization, in-plane anisotropy field, and gyromagnetic ratio were obtained on 1 μm thick films sputtered in a 50%

oxygen and 50% argon atmosphere. The films showed a large magnetization and anisotropy field at room temperature. The low temperature magnetization, Curie temperature, and gyromagnetic ratio were found to be in agreement with the values expected for crystalline copper ferrite. A paramagnetic to antiferromagnetic transition at 50 K was evident in the magnetization data. We proposed that the films contained magnetically ordered clusters of copper ferrite and Fe_2O_3.

"Magnetically ordered amorphous copper ferrite," G. Srinivasan, B. Uma Maheshwar Rao, J. Zhao, and M. S. Seehra, Appl. Phys. Lett. 59, 372 (19991).

II-G: FOLLOW-UP:

The primary focus of the follow-up work will be on the effects of superexchange interactions on ordering in noncrystalline compounds of spinel ferrites, transition metal oxides, and multilayers of oxides. Efforts would also be directed towards an understanding of the influence of sputtering parameters on the formation of ordered clusters in the amorphous state. Our studies reveal a critical dependence of the magnetization on the sputtering atmosphere. Collaborative Mossbauer, Raman Scattering, and off-resonance line-width studies will be performed on representative samples in order to understand the nature and composition of ordered clusters and high frequency losses in the amorphous state.

These studies will be funded by a grant from the American Chemical Society.

III. PUBLICATIONS:

1. "Magnetic properties of amorphous $BiFeO_3$ - $PbZrO_3$ sputtered films," B. Uma Maheswar Rao, G. Srinivasan, V. Suresh Babu, and M. S. Seehra, J. Appl. Phys. 69, 5463 (1991).
2. "Effects of high temperature annealing on amorphous $BiFeO_3$ with nonmagnetic substitutions," B. Uma Maheshwar Rao and G. Srinivasan, Appl. Phys. Lett. 59, 372 (1991).
3. "Magnetic ordering in amorphous films of $BiFeO_3$ - $ZnFe_2O_4$," B. Uma Maheshwar Rao and G. Srinivasan, Phys. Rev. B 44, 395 (1991).
4. "Magnetically ordered amorphous copper ferrite," G. Srinivasan, B. Uma Maheshwar Rao, J. Zhao, and M. S. Seehra, Appl. Phys. Lett. 59, 372 (19991).
5. "Static and high frequency magnetic properties of amorphous $BiFeO_3$ - $CuFe_2O_4$ compounds," B. Uma Maheshwar Rao and G. Srinivasan, J. Appl. Phys. 70, 6317 (1991).
6. "High Frequency Phenomena in Microwave Materials," G. Srinivasan and B. Uma Maheswara Rao, Concise Encyclopedia of Magnetic and Superconducting Materials, ed. Jan E. Evetts, Pergamon Press (contribution by invitation).
7. "Effects of sputtering atmospheres on magnetic properties of amorphous films of $BiFeO_3$ - $ZnFe_2O_4$," B. Uma Maheshwar Rao and G. Srinivasan, in press, Journal of Magnetism and Magnetic Materials.
8. "Magnetization and ferromagnetic resonance studies on rf sputtered amorphous $BiFeO_3$ - $CuFe_2O_4$ compounds," B. Uma Maheshwar Rao and G. Srinivasan, in press, Journal of Magnetism and Magnetic Materials.
9. "Magnetic properties of amorphous films of Bi_2O_3-Fe_2O_3-CaO," B. Uma Maheshwar Rao and G. Srinivasan, paper to be presented at INTERMAG'92. The manuscript if accepted will be published in IEEE Trans. Magn. 1992.

V. PERSONNEL:

The personnel supported on this project in one form or another (salary, materials, etc.,) are listed below.

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Undergraduate Students:	David Hagerty (B.S. Physics) Jeff Viola (B.S. Physics) Roger Hasse (B.S. Physics) Mike Houston (B.S. E.E) Mike Flaga (B.S. Physics) Manpreet Singh (B.S. Computer Sci.) Fahimeh Ghoujeghi (B.S. Computer Sci.)
High School Students:	Adolf Jones (Senior, Pontiac Central) Roy Colon (Senior, Pontiac Central)